Explaining the redox imbalance between the H and O escapes fluxes at Mars by the oxidation of methane

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Explaining the redox imbalance between the H and O escapes fluxes at Mars by the oxidation of methane

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Abstract

From a comparison between the different observations of Martian methane existing today ([1], [2], [3]), we show that all sets of data are globally consistent with each other, and that a well definite seasonal cycle of methane has been at work for at least 10 yr. With a simple model of the balance between the loss fluxes of H and O, using up-to-date values of the escape fluxes, we show that the long-standing enigma of the imbalance between H and O escape fluxes may be solved by assuming that the missing sink of oxygen is the oxidation of methane. If no H_2 is released together with CH_4, an excellent agreement is found between the present CH_4 flux and the value imposed by balance between H and O escape fluxes, an average over the last $\approx 10^3$ yr. If H_2 is released together with CH_4, as expected if CH_4 originates in serpentinization, the average level of CH_4 during the last 10^3 yr should have been at least ten times lower than the present one. The lack of present H_2 release could suggest a long-term storage of methane in the subsurface under the form of clathrates. We suggest that the thin layer of CO_2 ice covering the permanent southern polar cap could result from the release of methane since the end of the last obliquity transition (time scale : 1 Myr), at an average rate of 0.1 Mt yr^{-1}, consistent with the values derived from : (i) the present observations of methane (time scale : 10 yr), (ii) the estimate from the observed imbalance between the H and O escape fluxes (time scale : 1 kyr). If so, the present release of methane from subsurface clathrates would have acted at a constant rate since at least 3 Myr.

1. Main goal of the talk

The main goal of this talk is to address the still unsolved question of the present imbalance between the O and H escape fluxes, and to show that it brings new information on the history of methane over the last $\approx 10^3$ yr. The present O escape flux is at least four times smaller than the H escape flux [4]. Introducing a sink of oxygen at the surface, in addition to the escape flux at the top of the atmosphere, would allow solving the problem. We suggest that oxidation of methane may be the sink of oxygen equilibrating the redox budget of the atmosphere. First, we reassess the question of the correlation between water vapor and methane ([1], [5]), and its potential consequences (Fig. 1). Second, we present the principle of the old, still unanswered, question of the imbalance between the O and H escape fluxes. In a third step, we propose updated estimates of the H and O escape rates based on last results of observation and modelling. Assuming that serpentinization is at the origin of methane, therefore producing also molecular hydrogen, we propose a simple model of redox balance of the Martian atmosphere (Fig. 2). Finally, we assess the consequences of our model on the recent evolution, over the last 10^3 yr, of the methane release rate.

2. A few conclusions

From a comparison between the different observations of Martian methane existing today, including the TES methane data to be published soon [3], we show that all sets of data are globally consistent with each other. There is a definite seasonal behaviour of methane over the last three seasonal cycles, with more methane during northern spring and summer, and less during fall and winter (Fig. 1).

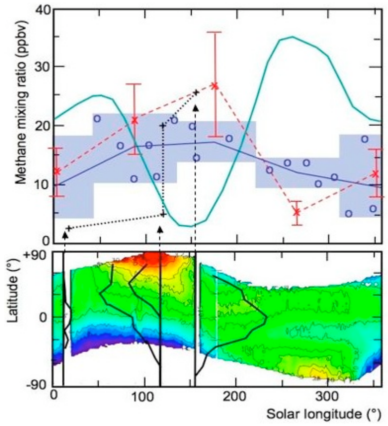

Fig. 1 : Upper panel : Seasonal evolution of the methane mixing ratio (red crosses and red dashed line : TES data, [3], blue circles : PFS data, [1]). The blue solid line connects the 4 points obtained by averaging PFS data in 4 bins : Ls= 0°±45°, 90°±45°, 180°±45° and 270°±45°, represented by the blue boxes. The average contents of methane measured from Hawaï [2] are also plotted (+ signs and black dotted line). The green-blue thick solid line gives the variation of the CO_2 pressure (in arbitrary units). Lower panel : TES water vapor map (Smith, 2004) and superimposed latitudinal profiles of methane measured from Hawai at three different seasonal dates [6]. The maximum of the methane profile at Ls=155° is ≈45 ppbv.

From a simple model of the balance between the loss fluxes of H and O (Fig. 2), we show that the long-standing enigma of the redox imbalance of escape fluxes may be solved by assuming that the missing sink of oxygen is the oxidation of methane. If no H_2 is assumed to be released together with CH_4, we find a good agreement, within less than a factor of 2, between the methane release flux calculated from observed mixing ratio (15 ppbv) and lifetime (200 days) and the value imposed by the redox balance between the loss fluxes of H and O. The absence of H_2 release would be consistent with the idea that methane is stored during a certain time under solid form (clathrate) in the subsurface, whereas H_2, which is volatile, is lost rapidly to the atmosphere as soon as it is formed.

Assuming that the layer of CO_2 present under ice form on the permanent south polar cap originate in the release of methane since 3 Myr, the time when tropical glaciers mostly disappeared, and water vapor from mid-latitudes stopped condensing on the southern polar cap, we find that the release rate of methane in the last 10^3 yr fits the rate required to explain the accumulation of the observed amount of CO_2 ice over the last 3 Myr. A release rate of methane of ≈0.1 Mt yr^{-1} is therefore consistent with three observational constraints : (i) the presently measured level of methane in the atmosphere of Mars (≈15 ppbv) and the estimate of its lifetime (6 months) (time scale : 10 yr), (ii) the redox imbalance between the O and H escapes fluxes (time scale : 1 kyr), (iii) the accumulated amount of CO_2 ice on the southern polar cap (time scale : 1 Myr).

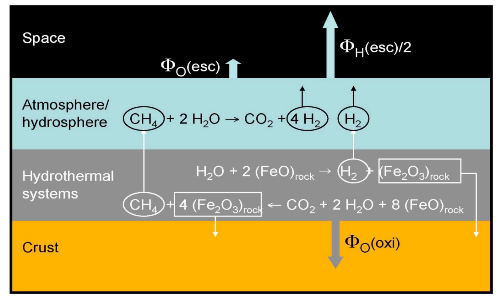

Fig. 2 : Schematic view of the carbon hydrothermal cycle from a redox point of view, showing the loss fluxes of oxygen and hydrogen from the active hydrosphere. Oxygen is lost through both escape [Φ_O(esc)] and ferric iron formation [Φ_O(oxy)]. Hydrogen is lost only by escape [Φ_H(esc)]. Due to the redox balance of the hydro-atmosphere, Φ_O(esc) + Φ_O(oxy) = ½ Φ_H(esc). Φ_H(esc)/2, which is the escape flux of H_2, is the sum of the O escape flux, Φ_O(esc), and the O loss flux to the crust, Φ_O(oxy).

References

[1] Geminale, A., Formisano, V., Giuranna, M. : Methane in Martian atmosphere: Average spatial, diurnal, and seasonal behaviour, Planet. Space Sci. 56, 1194-1203, 2008.
[2] Mumma, M. J., Villanueva, G. L., Novak, R. E., Hewagama, T., Bonev, B. P., DiSanti, M. A., Mandell, A. M., Smith, D. M., Strong Release of Methane on Mars in Northern Summer 2003, Science 323, 1041-1045, 2009.
[3] Fonti, S. and Marzo, G.A. : Mapping the methane on Mars, Astron. Astrophys., in press, 2010.
[4] Valeille A., Combi M.R., Bougher S.W., Tenishev V., Nagy, A.F : 3D study of Mars upper-thermosphere/ ionosphere and hot oxygen corona: (2) Solar cycle, seasonal variations and evolution over history, J. Geophys. Res., In press, 2009.
[5] Chassefière, E., Metastable methane clathrate particles as a source of methane to the Martian atmosphere, Icarus 204, 137-144, 2009.